



INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

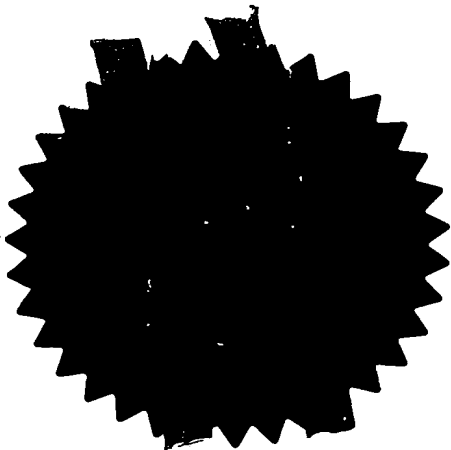
BEST AVAILABLE COPY

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

Andrew Gersey

Dated

24 January 2005

THE PATENT OFFICE
CR

Patents Form 1/77 17 DEC 2003

Patents Act 1997
(Rule 16)

RECEIVED BY FAX

The
Patent
Office

1/77

Request for grant of a patent*(see the notes on the back of this form. You can also get an explanatory leaflet from the Patent office to help you fill in this form)*

17 DEC 2003

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1 Your reference

TEC 51125/GB

2 Patent application number
(The Patent Office will fill in this part)

0329208.3

3 Full name, address and postcode of the or of
each applicant (underline all surnames)Imperial Chemical Industries plc
20 Manchester Square
London
W1U 3AN

Patents ADP Number (if you know it)

0000093506

If the applicant is a corporate body, give the
country/state of its incorporation

United Kingdom

935006

4 Title of the invention

Particulate Materials

5 Name of Your Agent (if you have one)

GRAHAM, John George MARTYN HUMPHRIES.

"Address for service" in the United Kingdom
to which all correspondence should be sent
(including the postcode)Uniqema Intellectual Property Dept
Wilton Centre, Wilton
Redcar
Cleveland
England, TS10 4RF

Patents ADP Number (if you know it)

7896889002

6 If you are declaring priority from one or more
earlier patent applications, give the country
and the date of filing of the or each of these

Country	Priority Application number (if you know it)	Date of Filing (day / month / year)
---------	---	--

7 If this application is divided or otherwise derived from an
earlier UK application, give the number and filing date of
the earlier application

Number of earlier application	Date of Filing (day / month / year)
-------------------------------	--

8 Is a statement of inventorship and of right to grant of a
patent required in support of this request?

Yes

Answer yes if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

See Note (d)

Patents Form 1/77

Patents Form 1/77

- 9 Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form -

Description 16

Claim(s) 4

Abstract -

Drawings 6

- 10 If you are also filing any of the following state how many against each item

Priority documents

Translations of priority documents

Statement of Invention and right to grant of a patent (Patents Form 7/77)

Request for Preliminary Examination and search (Patents Form 9/77)

Request for Substantive Examination (Patents Form 10/77)

Any other documents (Please specify)

11

I/We request the grant of a patent on the basis of this application

Signature

John George GRAHAM

Date

17 Dec 2003

- 12 Name and daytime telephone number of person to contact in the United Kingdom

John George GRAHAM
01642 435335

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been issued, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

Patents Form 1/77

Applicant's Reference TEC 51125

1

Particulate Materials

This invention relates to particulate materials and methods of producing particulate materials.

Particulate materials have found utility in a wide range of applications. For example, encapsulated fragrances and flavours (organoleptics) are widely used in the food/nutrition, home care, eg laundry, and personal care (including cosmetic) fields. Other encapsulated actives, such as biocides, are widely used in the agriculture and hygiene fields. Encapsulated pharmaceutical preparations that permit slow or controlled release of the active ingredient have been widely used. New applications in electronics materials are also generating significant interest.

Particulate materials in which active ingredients are encapsulated within carrier or matrix materials enables the actives to be handled easily and to be readily incorporated within other systems to be dispersed or released, in use, to permit the active ingredient to have its effect. Thus, effective protection of the actives until required, long shelf life, size and density and the controlled or phased release of the active are very important factors in whether such particulate materials are commercially attractive. For example, a wide particle size range may result in a poor dispersion/dissolution of the particles and hence the active in use; or the separating out of the particulate material containing the active ingredient from other particulate materials in a mixture, eg in laundry powders, would be detrimental to the even dispersion of the active in use.

Such particulate materials are generally produced from a liquid precursor by spraying the liquid precursor and, depending on the precursor, either drying it or cooling it to form the particulate materials. The liquid precursor may typically be a melt of a polymer matrix material in which is dispersed an active ingredient in which case the sprayed material is chilled to cause it to at least partially solidify during flight to form spherical particles. Alternatively, the liquid precursor may be a solution or emulsion containing the matrix material and the active ingredient and it is subjected to conditions such as heat to dry it or cause some other phase change sufficient to form the particles during flight.

Spray dryers or chillers are well known and typically consist of a tower into which the liquid precursor is sprayed by an atomiser and in which the liquid droplets are subjected to a gas flow, either co-current or counter-current, to effect at least a partial

Applicant's Reference TEC 51125

2

phase change in the droplets. Commonly used atomisers are single fluid nozzles, two-fluid pneumatic nozzles and high speed rotary disc atomisers. Examples of such spray dryers/atomisers can be found in US-B-5545380, US-B-564530, US-B-6531444 and US-A1-2002/0071871. However, such spray equipment tends to

5 produce a relatively wide particle size distribution, including a significant proportion of fines, ie particles with a size less than 30 μm . Although it is possible to refine the size distribution by classifying the particles using screens, cyclone separators etc, the use of such techniques adds significantly to the cost of manufacturing the particulate materials.

10 Other forms of equipment use different techniques to produce particulate material in which the particle size range is relatively narrow, ie the particles are said to be substantially mono-dispersed. The techniques include applying fluctuating pressure to the liquid being atomised and mechanically or acoustically perturbing the jets of liquid to break them up into droplets. Examples of such equipment can be found in

15 US-A-4585167, GB-A-1454597, EP-A-86704, EP-A-320153 and WO 94/20204. Such equipment has been primarily used to form relatively large prills from a molten precursor such as molten ammonium nitrate.

Particulate materials having a relatively narrow particle size distribution may have advantages over particulate materials having relatively wide particle size

20 distributions. For example, particulate materials having a relatively narrow particle size distribution tend to be less dusty, are free flowing and more easily metered and are safer to handle. However, the Applicant has been found that, even with particulate materials having a relatively narrow particle size distribution, significant difficulties may be experienced in dispersing the particles in liquids in use.

25 Additionally, wetting of the particles by liquids in use and release of the active ingredient is frequently very variable. Those variables are disadvantageous in many applications as they may give rise to poor or incomplete release of the active ingredient in applications such as crop adjuvants, instant foods and laundry products or leave unattractive residues in deodorant/anti-perspirant applications. These

30 issues do not appear to have previously been addressed.

Investigation made by the Applicant has shown that the problems arise owing to the presence in known particulate materials of mixed morphologies. The exception to this is particulate materials produced by spray chilling molten precursor material wherein surface tension effects in the molten droplets tends to produce a

35 substantially spherical morphology. However, in particulate materials formed by

Applicant's Reference TEC 51125

3

spray drying, the Applicant has been found that mixtures of morphologies are present in the particulate material. The morphologies that have been found are:

- 5 spherical
 hollow sphere
 roughly spherical
 cenospheres
 packed porous network.

10 The morphologies are described in more detail below. The Applicant has found the density of the particles and the release of the active ingredients from the particles is dependent on the morphologies of the particles. Thus, the presence of significant amounts of differing morphologies in the particulate material results in non-uniform release of the active ingredient which situation is exacerbated by the presence of a relatively wide spread of particle sizes. Even in substantially homogeneous particulate materials, the dispersibility and dissolution of the material is non-uniform.

15 The Applicant has found that, surprisingly, by the selection of the production method and the parameters under which the particles are generated, it is possible to make particulate material having a selected morphology when more than one morphology is capable of being produced.

20 Accordingly, it is an object of the present invention to provide particulate material made by a spray process in which the particles are substantially mono-dispersed and have substantially the same morphology.

It is another object of the present invention to provide a process for making particulate material in which the particles are mono-dispersed and have substantially the same morphology.

25 According to a first aspect of the present invention, a particulate material made by a spray process has at least 80%, preferably at least 90% and more especially at least 95% of the particles of the same morphology, said particulate material having a mono-dispersivity index of not more than 1.2, preferably not more than 1.0 and more especially not more than 0.6.

30 According to a second aspect of the present invention, a particulate material made by a spray process has at least 80%, preferably at least 90% and more especially at least 95% of the particles of the same morphology, said particles having at least two

Applicant's Reference TEC 51125

4

components, a first component being at least one matrix material and a second component being at least one active ingredient retained by said first component, and said particulate material having a mono-dispersivity index of not more than 1.2, preferably not more than 1.0 and more especially not more than 0.6.

- 5 Although all of the previously mentioned morphologies can be generated in the particulate material of the present invention, it is preferred that particles have a morphology selected from hollow sphere, roughly spherical, cenospheres and packed porous network morphologies.

The mono-dispersivity index (MDI) is determined as follows:

10
$$\text{MDI} = \frac{(\text{particle size } 90\%) - (\text{particle size } 10\%)}{(\text{particle size } 50\%)}$$

where:

- 15 (particle size 90%) is the size below which 90% by volume of the particles lie;
(particle size 10%) is the size below which 10% by volume of the particles lie;
and
(particle size 50%) is the size below which 50% by volume of the particles lie.

- Although ideally, the MDI is as small as possible preferably approaches zero, from a practical point of view, the particulate material according to the invention has an MDI
20 of greater than 0.05 and is more typically greater than 0.1, and is usually greater than 0.2.

Preferably, the particulate material according to the invention comprises particles that are substantially all of the same morphology, ie substantially 100% of the particles are of a particular morphology.

- 25 Preferably, the particulate material according to the invention comprises particles having a volume mean size in the range 50 μm to 3000 μm . The lower end of the volume mean size range is 50 μm and more preferably 100 μm . The upper end of the volume mean size range is 3000 μm and more preferably 2000 μm and more especially 1000 μm . Preferably, the particulate material comprises particles having a
30 volume mean size in the range 100 μm to 600 μm , more especially 200 μm to 500 μm .

Preferably, the particulate material according to the invention is essentially dust free by which is meant it essentially does not contain any particles having a volume mean size less than 20 μm ; more preferably it essentially does not contain any particles having sizes less than 50 μm and especially it essentially does not contain any particles having a volume mean size less than 80 μm . It will be understood this reference to the particulate material being essentially dust free is to the particulate material as made. In other words, it is not necessary to subject the particulate material according to the invention to a subsequent processing step to remove fines.

In the particulate material according to the invention, the particles, if homogeneous, or the first component and second components of the particles, if heterogeneous, may be selected from a wide range of materials depending on the application in which the particulate material is to be used.

When the particles are heterogeneous, the materials from which the first component is selected will enable the second component to be retained thereby, for example through encapsulation or binding together, to form discrete particles.

In some applications, the first component forms a material network that has interstices in which the second component is held. Such matrices may be inorganic or organic crystalline structures or may be amorphous or glassy-like structures. Examples of such matrices include inorganic salts such as sulphates, nitrates, acetates, carbonates etc and organic materials such as lactose, starches, sugars and organic acids.

In many applications, the particles have to be biocompatible. In particular, when the particles are heterogeneous, the first component has to be biocompatible. By "biocompatible" is meant that users of products containing the particulate material according to the invention experience no adverse affects. Examples of such uses are the use of encapsulated organoleptics in food, personal care and home care applications.

Suitable biocompatible materials for use as the first component may be selected from sugars, polysaccharides, starches and glycerides, especially di- and tri-glycerides. Such materials are also film forming.

Other applications may require the material of the particles, or when heterogeneous, the material of the first component to be film forming. Examples of such materials are polyvinyl acetate and ethylene vinyl acetate copolymers including mixture thereof

Applicant's Reference TEC 51125

6

with each other or with other materials such as latex, waxes, fats, lipids, and biopolymers.

5 In the particulate material according to the invention, when the particles are heterogeneous, the second component of the particles may be selected from a wide range of materials depending on the application in which the particulate material is to be used. The materials from which the second component are selected will be compatible with the first component in the sense of being non-reactive with the first component, at least in the particles and the precursor formulations from which the particles are derived.

10 In the particulate material according to the invention, the second component of the particles may be selected from organoleptics, nanoscale fillers such as inorganic fine oxides, catalysts, skin benefit agents, nutrients, responsive polymers such as hydrogels.

15 In fragrance and flavour terms, the preferred organoleptic components are those that are most susceptible to attack without the protection offered by encapsulation e.g. highly volatile molecules, essential oils and fragrance chemicals which are susceptible to oxidative attack when used in bleach containing detergents.

20 Hydrogels are polymers that absorb liquids and swell. The polymer chains are tangled and form porous networks similar to micro-sponges. Hydrogel particles are used to absorb the active ingredient and are then dispersed in a matrix material and subjected to a spray process to form particulate material according to the present invention. Polymers that form hydrogels typically contain hydroxyl, amine, amide, ether, carboxylate or sulphate groups or combinations of such groups. Typical of such polymers is α , β -poly (N-2-hydroxyethyl)-DL-aspartamide.

25 In the particulate material according to the invention, when the particles are heterogeneous, the second component of the particles may in itself be a binary or higher order particle. For example, the second component may be an active material encapsulated by a matrix to form a core shell particle. Examples of matrix materials are maltodextrin, starches, sugars, polysaccharides and fats.

30 More generally, examples of matrix-forming materials are:

- starch, chemically and/or physically modified starch, starch systems containing other carbohydrates and/or polyols as described in EP 0 922 449

Applicant's Reference TEC 51125

7

A2, US 5,185,176; 4,977,252; 3,971,852, EP 0550067 (also, Modified Starches: Properties and Uses, O.B.Wurzburg, editor, CRC Press, Boca Raton, Florida (1986).). Starch/oil composites (US 5,882,713 and 5,676,994);

- 5
 - cellulose and cellulose derivatives (e.g. hydroxypropyl cellulose, carboxymethyl cellulose), alginate esters, alginic acid, carrageenans, agar, pectinic acids, plant gums or exudate gums (e.g. gum arabic, gum tragacanth and gum ghatti); hemicelluloses (cell wall polysaccharides such as D-xylans, L-Arabino-D-xylans, D-mannans, D-galacto-D-mannans and D-gluc-D-mannans);
- 10
 - cyclodextrins and their derivatives;
 - polyvinyl alcohols, polyethylene glycols, polyvinyl pyrrolidones, polyacrylic acid and its derivatives, polyacrylamides, poly(ethylene oxides), styrene maleic anhydride copolymers, poly(vinyl sulfonic acids) (e.g. see US 4,209,417; 4,339,356; 3,576,760). Other synthetic materials include
- 15
 - polyurethanes, polyureas, melamine resins, melamine / urea resin;
 - gelatin, soy protein, whey protein, gelatin / gum Arabic; and
 - absorption of actives into inorganic particulates such as silicas, clays, zeolites followed by coating with any of the polymeric systems described above (e.g. see WO 02/064725, WO 01/40430A1); and
- 20

examples of active ingredients are:

 - oils, fats, flavors, fragrances, vitamins, pharmaceuticals, inorganic or organic fillers, sunscreens, moisturizers, substances or mixtures that accomplish a pest control function, oil field additives, enzymes, hair conditioners and skin conditioners.
- 25

Preferably, in the particulate material of the present invention, when the particles are heterogeneous, the second component comprises between 30 wt% to 50 wt% of the particles.

A preferred embodiment of the present invention, when the particles are heterogeneous, comprises the first component being at least one matrix material
- 30

selected from sugars, polysaccharides, starches and glycerides, especially di- and

Applicant's Reference TEC 51125

8

tri-glycerides, and a second component being at least one active ingredient retained by said first component and being an organoleptics.

Another preferred embodiment of the present invention, when the particles are heterogeneous, comprises the first component being at least one film-forming polymeric matrix material.

In terms of applications, slow dissolution of the particles and/or dispersion of active ingredients therein may be achieved by selecting film-forming materials and morphologies, ie spherical, hollow spheres and cenospheres; medium dissolution of the particles and/or dispersion of active ingredients therein may be achieved by selecting particles having a morphology suited to erosion mechanisms, ie roughly spherical; and fast dissolution of the particles and/or dispersion of active ingredients therein may be achieved by selecting the packed porous network morphology.

According to another aspect of the invention, the particulate material according to the present invention is made by projecting from a body of liquid comprising a precursor formulation for said particulate material an array of mutually divergent jets, disturbing the jets to cause break up thereof into streams of droplets of narrow size distribution, contacting the array of resulting droplet streams with a gas flow to reduce coalescence of the droplets in each stream and causing or allowing the droplets to solidify at least partially in flight, wherein said precursor formulation has a density in the range 1000 kg/m^3 to 1700 kg/m^3 , a viscosity in the range 0.06 Pa.s to 1 Pa.s and a surface tension in the range 0.03 N/m to 0.72 N/m and an Ohnesorge Number in the range 0.005 to 1 , more especially in the range 0.008 to 1 and wherein the liquid jets have a Reynolds Number (Re_j) in the range 50 to 5000 , more especially in the range 50 to 2000 and wherein the volume mean droplet size produced is in the range $50 \text{ }\mu\text{m}$ to $3000 \text{ }\mu\text{m}$.

The process, and apparatus in which the process may be carried out, is particularly described in WO 94/20204, which is incorporated herein by reference in its entirety.

As described in WO 94/20204, the divergent jets may be disturbed to cause break up thereof by mechanical or acoustic vibration. In the method according to the present invention, the divergent jets are preferably disturbed to cause break up thereof by acoustic vibration. Preferably, the Weber frequency (f_w) used for droplet generation is in the range 0.5 kHz to 100 kHz . Preferably, the flow in the jets is laminar.

Applicant's Reference TEC 51125

9

A preferred embodiment of the method of the present invention, when the particles are heterogeneous and in which the first component is at least one matrix material selected from sugars, polysaccharides, starches and glycerides, especially di- and tri-glycerides comprises the liquid jets having a Re_j in the range 50 to 5000 and the drops are generated using an fw in the range 2 kHz to 15 kHz.

Another preferred embodiment of the method of the present invention, when the particles are heterogeneous and in which the first component is at least one film-forming polymeric matrix material comprises the liquid jets having a Re_j in the range 10 to 50 and the drops are generated using an fw in the range 10 kHz to 100 kHz.

Yet another preferred embodiment of the method of the present invention, when the particles are heterogeneous and wherein a material network is formed comprises the liquid jets having a Re_j in the range 50 to 1000 and the drops are generated using an fw in the range 2 kHz to 50 kHz.

The present invention will now be described by way of example only with reference to the accompanying drawings in which:

Figure 1 is a schematic view of particle morphology formation;

Figure 2 is a schematic view of spraying apparatus;

Figure 3 is a micrograph of the particulate material of sample 1 described in Example 1;

Figure 4 is a micrograph of the particulate material of sample 2 described in Example 1;

Figure 5 is a micrograph of the particulate material of sample 4 described in Example 1;

Figure 6 is a micrograph of the particulate material of sample 5 described in Example 1;

Figure 7 is a micrograph of the particulate material of sample 6 described in Example 2;

Figure 8 is a micrograph of the particulate material of sample 6 described in Example 2 taken at a higher magnification;

Applicant's Reference TEC 51125**10**

Figure 9 is a micrograph of the particulate material of sample 12 described in Example 2;

Figures 10 and 11 are micrographs of the particulate material of sample 12 described in Example 2 taken at a higher magnification; and

5 Figures 12 and 14 are micrographs similar to Figures 9 to 11 but of the particulate material of sample 11 described in Example 2..

As mentioned above, the morphologies are identified as:

- spherical**
- hollow sphere**
- 10 roughly spherical**
- cenospheres**
- packed porous network.**

Referring to Figure 1, the particulate material of the present invention preferably comprises particles of one of the morphologies shown. As shown, as the droplet is
15 subjected to the gas flow, a crust is formed and each particle is then able to adopt one of the morphologies shown or a spherical morphology (not shown).

In the hollow sphere morphology, the particles generally have a shape close to or actually spherical and are hollow.

**The roughly spherical morphology has particles that are generally round, ie sphere-
20 like, in shape but they do not have a smooth surface. The surface appearance can vary from slightly rough, almost scale-like in appearance to very rough, irregular and knobbly or protrusion-covered surfaces. The particles are solid apart from a very small irregular central cavity, which arises as a result of density differences between the precursor formulation and the particle.**

25 In the cenospheres morphology, the particles generally have a shape close to a sphere but are more likely to be slightly elongate or elliptical in appearance as compared to a true sphere and have an opening through the shell into the hollow centre.

**As indicated in Figure 1, the particle density varies across the morphologies as does
30 the release mechanism of the active from the matrix.**

In terms of applications, slow dissolution of the particles and/or dispersion of active ingredients therein may be achieved by selecting film-forming materials and morphologies, ie spherical, hollow spheres and cenospheres; medium dissolution of the particles and/or dispersion of active ingredients therein may be achieved by
5 selecting particles having a morphology suited to erosion mechanisms, ie roughly spherical; and fast dissolution of the particles and/or dispersion of active ingredients therein may be achieved by selecting the packed porous network morphology.

A spherical morphology would be similar to the hollow sphere morphology shown in Figure 1 except that it would be solid apart from a very small irregular central cavity,
10 which arises as a result of density differences between the precursor formulation and the particle. In this instance, the particle would have high density and the release would be erosion controlled.

Referring to Figure 2, spraying apparatus 10 has a spray tower 12 at the top of which is located a spray head (not shown). A feed line 14 supplies a precursor formulation
15 to the spray head and a gas supply line 16 provides gas via a heater or cooler 18 to the tower 12 for the gas to impinge on droplet streams emitted from the spray head. An exhaust line 20 feeds the particles and exhaust gas to a separator 22 from which products off take 24 and a gas exhaust 28 exit.

As shown, the gas flow is concurrent with the droplet streams. In other
20 arrangements, the gas flow may be counter-current with the gas entering the lower section of the spray tower 12 and being exhausted at its upper end above the spray head.

The spray head (not shown) may be a nozzle or rotary atomiser in conventional spray drying; alternatively, in accordance with the present invention, it is an acoustic
25 spray head of the type described in WO 94/20204.

The invention will now be illustrated further with reference to the following Examples.

The following tests were performed on the samples:

bulk density measurement
dispersibility
30 SEM micrographies
water amount measurement
retention of active

Applicant's Reference TEC 51125

12

volume mean size.

The tests were carried out as follows:

Bulk density

5 The following process was used to measure the bulk density of the spray-dried particulate material. A 100 ml beaker was weighted empty. Particulate material was added to the beaker, which was then tapped and shaken manually to cause the particles to settle and compact. This step was iterated until no further volume change was observed. The now full beaker was weighed. The weight of the empty beaker was subtracted from the weight of the full beaker to obtain the weight of the
10 particulate material in the beaker and the bulk density was then calculated by dividing the weight (in kilograms) by 10^{-4} (the volume of the beaker in m^3).

Dispersibility in water

15 A measured amount of particulate material, approximately 1g, was poured into a beaker containing a 200g of demineralised water and its capacity to be completely dissolved or, on the contrary, to remain in particulate form or to aggregate into lumps was observed, together with the time needed to achieve the final condition.

Water amount measurement

20 The water amount in a material can highly influence its physical and chemical properties, causing for example its plasticisation and consequently reducing its glass transition temperature. In the Examples, the test was carried out to measure the residual moisture in the particulate material to enable an appropriate correction to be made to the measured active ingredient retention, which is at least partly dependent on this variable.

25 The moisture content of the particulate material was measured using a Karl-Fisher water measurement apparatus. To determine the moisture content in a non-aqueous solvent for the particulate material, ie ethanol, 100 μ litres of ethanol was injected into the apparatus and the moisture content of the solvent was measured. Using the same solvent batch, a measured amount, around 1 mg, of particulate material was dissolved in ethanol and 100 μ litres of the solution was injected into the Karl-Fisher
30 apparatus and the moisture content of the solvent was measured. As the amount of water in the pure solvent and in the solution are known and the exact weight of the

dissolved and injected particulate material is known, the residual moisture in the sample can be calculated.

Retention of active ingredient

5 In each test, 15 g of particulate material, together with several drops of silicon (as an antifoaming agent) and some boiling chips, were dispersed in 250 ml demineralised water in a distillation apparatus. The mixture was heated until the mixture was boiling. Heat was then applied to the mixture to maintain it at boiling temperature of the mixture for three hours. The apparatus was then allowed to cool to room temperature and the height of oil collected in the distillate collection column was
10 measured using a precision calliper, and the percentage of oil retained was calculated using the formula:

$$\% \text{ retention} = \frac{(\text{X ml distillate})(\text{specific gravity distillate})}{(\% \text{w/w load})(\text{dry weight particulate material})} (100)(1.04)$$

15 The (1.04) in the formula is a correction factor for residual moisture, in this instance 4%.

Example 1

In this Example, a modified food starch derived from waxy maize sold under the trade name HI-CAP 100 by National Starch & Chemical Company, USA was used to make
20 particulate materials according to the invention. This particular product has been found to be especially suited for the encapsulation of flavours, clouds, vitamins and spices, at high oil loading using other encapsulation techniques.

In this Example, the particulate material was made only using the HI-CAP 100. The HI-CAP 100 is formed into an emulsion which is then subjected to a spray process.
25 The emulsion was prepared following the recommended procedure to prepare an emulsion of HI-CAP 100, namely:

1. disperse HI-CAP 100 in water at ambient temperature with good agitation;
2. heat the dispersion preferably with agitation to 82°C to ensure the HI-CAP 100 is completely dispersed;
30
3. cool the solution to ambient temperature.

Several solutions were made using HI-CAP 100 at solid concentration of 25%, 35% and 45% by weight, the balance being water.

The emulsions were then each subjected to a spray process using apparatus shown schematically in Figure 2 and more specifically described in WO 94/20204. The process conditions of inlet and outlet temperature, as well as jets number and size for each sample are described in Table 1.

Table 1

Sample	Cs %	Jet Reynolds No	Inlet T °C	Outlet T °C	Jets n# x size [μm]
1	25%	Approx 150	250	130	25 x 120
2	35%	Approx 240	210	120	15 x 150
3	45%	Approx 240	210	110	20 x 150
4	35%	Approx 150	210	110	30 x 120
5	35%	Approx 150	230	128	30 x 120

The bulk density of the samples were measured as described above and the results are shown in Table 2.

Table 2

Sample	Density [kg/m ³]
1	340
2	460
3	340
4	450
5	400

All of the samples were tested for dispersibility as described above. All of the particulate material dispersed well in the water within a few minutes, there being no discernable amounts of particulate material present whether as added or aggregating in clumps.

Reference is now made to Figures 3 to 6.

The particles sizes are in the range from 250 to 500 microns depending on the nozzles used.

Applicant's Reference TEC 51125

15

In Figures 3 and 4 (Samples 1 and 2, respectively), roughly spherical morphologies are exhibited by the particulate material, each morphology being at the extreme of roughly spherical.

5 In Figure 5, spherical morphology is exhibited and in Figure 6 cenospherical morphology is exhibited.

Example 2

Further samples of particulate materials according to the invention were made in accordance with the procedure described in Example 1, with the exception that an active ingredient was added to the process. The active ingredient was orange oil –

10 Givaudan orange oil: code 705820, Single Fold, Citrus Valley Blend available from Quest Foods, Naarden, Holland. In making the emulsion, the orange oil was added after step 3 with suitable agitation to disperse it in the water/starch solution, which dispersion was then subjected to an emulsification process using a Silverson mixer to create an emulsion in which the oil particles were of the order of 1 to 2 μm . The

15 parts by weight of the components in the emulsion were as shown in Table 3.

Table 3

Ingredient	Parts by Weight
HI-CAP 100 34	24
Orange Oil	16
Water	60

A number of samples of particulate material were generated using the conditions recorded in Table 4.

20 Table 4

Sample	Inlet T °C	Outlet T °C	Jet n# x size [μm]
6	190	108	16 x 200
7	215	102	16 x 200
8	190	98	30 x 150
9	200	108	25 x 150
10	250	120	25 x 150
11	215	110	25 x 150
12	210	116	15 x 150
13	210	120	15 x 200
14	220	115	15 x 200

Applicant's Reference TEC 51125

16

15	190	112	15 x 120
16	200	107	20 x 120
17	180	89	15 x 200

The bulk density, orange oil retention and residual moisture content were determined as described above and the results are shown in Table 5.

Table 5

Sample	Density (g/cm ³)	Orange Oil Retention %	Residual moisture %
6	480	93.40	3.6
7	510	89.80	4.48
8	470	98.40	2.7
9	430	93.50	3.0
10	450	95.80	2.9
11	270	97.50	2.57
12	500	94.40	2.83
13	500	94.36	3.1
14	450	95.60	3.3
15	440	96.60	2.60
16	470	98.20	2.58
17	295	94.80	2.63
18	530	89.20	4.70

5

Reference is now made to Figures 7 to 11.

In Figures 7 and 8 (Sample 6), the particulate material exhibits hollow spherical morphology, the encapsulated oil particles clearly being visible in the wall structure of the hollow spherical particle.

- 10 In Figures 9 to 11, the particulate material exhibits roughly spherical morphology, the encapsulated oil particles clearly being visible in the wall structure of the roughly spherical particle.

- 15 In Figures 12 to 14, the particulate material exhibits cenospherical morphology, the encapsulated oil particles clearly being visible in the wall structure of the cenospherical particle.

Applicant's Reference TEC 51125

17

Claims

1. A particulate material made by a spray process has at least 80%, preferably at least 90% and more especially at least 95% of the particles of the same morphology, said particulate material having a mono-dispersivity index of not more than 1.2, preferably not more than 1.0 and more especially not more than 0.6.
2. A particulate material made by a spray process has at least 80%, preferably at least 90% and more especially at least 95% of the particles of the same morphology, said particles having at least two components, a first component being at least one matrix material and a second component being at least one active ingredient retained by said first component, and said particulate material having a mono-dispersivity index of not more than 1.2, preferably not more than 1.0 and more especially not more than 0.6.
3. A particulate material according to claim 1 or claim 2 in which the particles have a morphology selected from hollow sphere, roughly spherical, cenospheres and packed porous network morphologies.
4. A particulate material according to any one of the preceding claims in which the particles have a mono-dispersivity index of greater than 0.05 and is more typically greater than 0.1, and is usually greater than 0.2.
5. A particulate material according to any one of the preceding claims in comprising particles that are substantially all of the same morphology
6. A particulate material according to any one of the preceding claims comprising particles having a volume mean size in the range 50 μm to 3000 μm .
7. A particulate material according to claim 6 comprising particles having a volume mean size in the range 100 μm to 2000 μm and more especially in the range 100 μm to 1000 μm .

Applicant's Reference TEC 51125

18

8. A particulate material according to claim 6 or claim 7 comprising particles having a volume mean size in the range 100 μm to 600 μm , more especially 200 μm to 500 μm .
- 5 9. A particulate material according to any one of the preceding claims which is essentially dust free.
- 10 10. A particulate material according to any one of the preceding claims which essentially does not contain any particles having a volume mean size less than 20 μm ; more preferably essentially does not contain any particles having sizes less than 50 μm and especially essentially does not contain any particles having a volume mean size less than 80 μm .
- 15 11. A particulate material according to any one of the preceding claims in which the particles are biocompatible.
- 20 12. A particulate material according to claim 11 in which the particles or the first component thereof are selected from sugars, polysaccharides, starches and glycerides, especially di- and tri-glycerides.
- 25 13. A particulate material according to any one of the preceding claims in which the material from which the particles or the first component thereof is made is film forming.
- 30 14. A particulate material according to claim 13 in which the first component is selected from polyvinyl acetate and ethylene vinyl acetate copolymers including mixture thereof with each other or with other materials such as latex, waxes, fats, lipids, and biopolymers.
- 35 15. A particulate material according to claim 2 or according to any one of the preceding claims dependent on claim 2 in which the first component forms a material network that has interstices in which the second component is held.
16. A particulate material according to claim 2 or according to any one of the preceding claims dependent on claim 2 in which the second component is selected from materials that are compatible with the first component.

Applicant's Reference TEC 51125

19

17. A particulate material according to claim 2 or according to any one of the preceding claims dependent on claim 2 in which the second component of the particles is a binary or higher order particle.
- 5
18. A particulate material according to claim 2 or according to any one of the preceding claims dependent on claim 2 in which the second component comprises between 30 wt% to 50 wt% of the particles.
- 10
19. A particulate material according to claim 2 or according to any one of the preceding claims dependent on claim 2 which comprises the first component being at least one matrix material selected from sugars, polysaccharides, starches and glycerides, especially di- and tri-glycerides, and the second component being at least one active ingredient retained by said first component and being an organoleptic.
- 15
20. A particulate material according to claim 2 or according to any one of the preceding claims dependent on claim 2 which comprises the first component being at least one film-forming polymeric matrix material.
- 20
21. A method of making a particulate material according to any one of the preceding claims comprising projecting from a body of liquid comprising a precursor formulation for said particulate material an array of mutually divergent jets, disturbing the jets to cause break up thereof into streams of droplets of narrow size distribution, contacting the array of resulting droplet streams with a gas flow to reduce coalescence of the droplets in each stream and causing or allowing the droplets to solidify at least partially in flight, wherein said precursor formulation has a density in the range 1000 kg/m^3 to 1700 kg/m^3 , a viscosity in the range 0.06 Pa.s to 1 Pa.s and a surface tension in the range 0.03 N/m to 0.72 N/m and an Ohnesorge Number in the range 0.005 to 1 , more especially in the range 0.008 to 1 and wherein the liquid jets have a Reynolds Number (Re_l) in the range 50 to 5000 , more especially in the range 50 to 2000 and wherein the volume mean droplet size produced is in the range $50 \text{ }\mu\text{m}$ to $3000 \text{ }\mu\text{m}$.
- 25
- 30
- 35
22. A method according to claim 21 in which the divergent jets are disturbed to cause break up thereof by acoustic vibration.

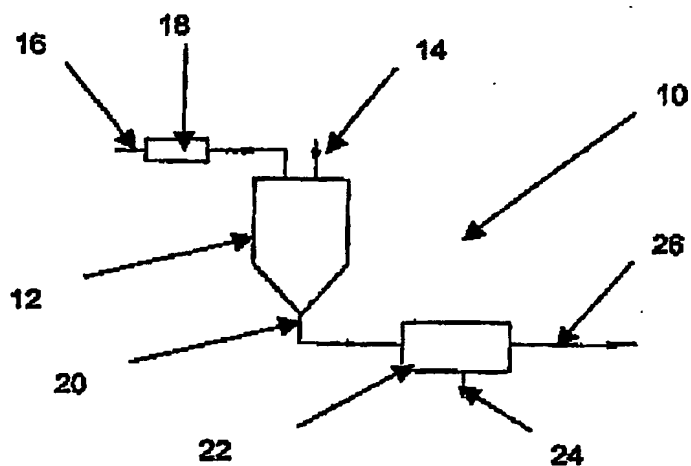
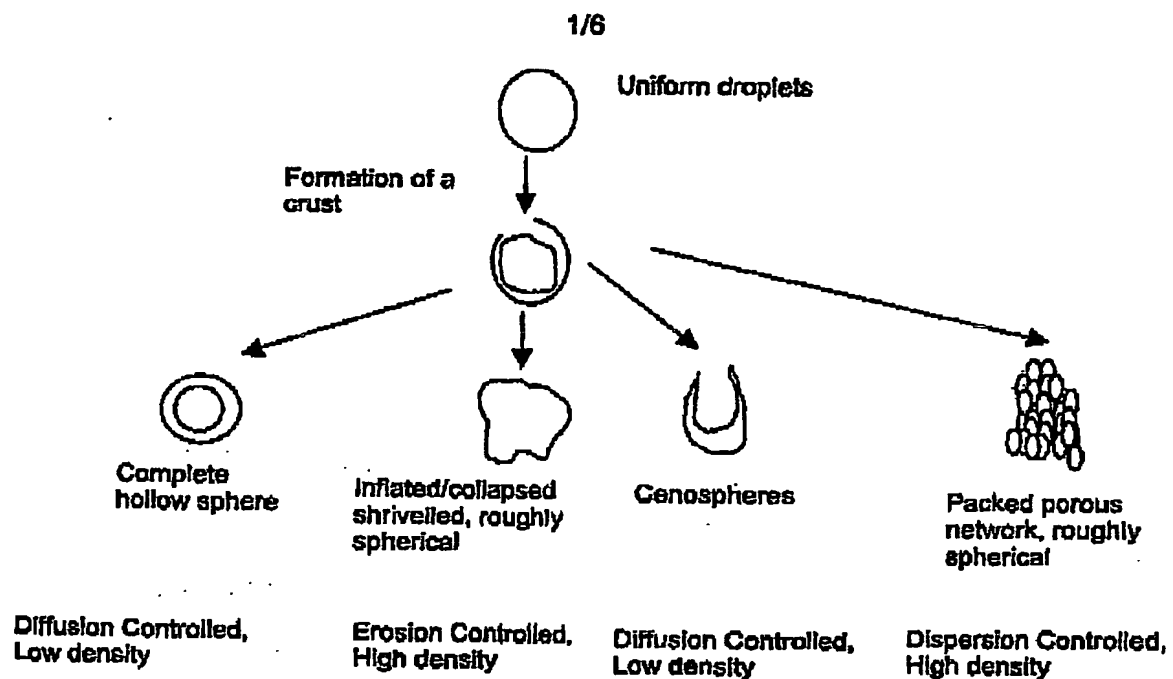
Applicant's Reference TEC 51125

20

23. A method according to claim 22 in which the Weber frequency (fw) used for droplet generation is in the range 0.5 kHz to 100 kHz.
- 5 24. A method according to any one of claims 21 to 23 in which the flow in the jets is laminar.
- 10 25. A method according to any one of claims 21 to 24 in which, when the particles comprise first and second components, the first component is at least one matrix material selected from sugars, polysaccharides, starches and glycerides, especially di- and tri-glycerides and the method comprises the liquid jets having a Re_j in the range 50 to 5000 and the drops are generated using an fw in the range 2 kHz to 15 kHz.
- 15 26. A method according to any one of claims 21 to 25 in which, when the particles comprise first and second components, the first component is at least one film-forming polymeric matrix material and the method comprises the liquid jets having a Re_j in the range 10 to 50 and the drops are generated using an fw in the range 10 kHz to 100 kHz.
- 20 27. A method according to any one of claims 21 to 25 wherein a material network is formed comprises the liquid jets having a Re_j in the range 50 to 1000 and the drops are generated using an fw in the range 2 kHz to 50 kHz.

25

Applicant's Reference TEC 51125



Applicant's Reference TEC 51125

2/6

Figure 3



Figure 4



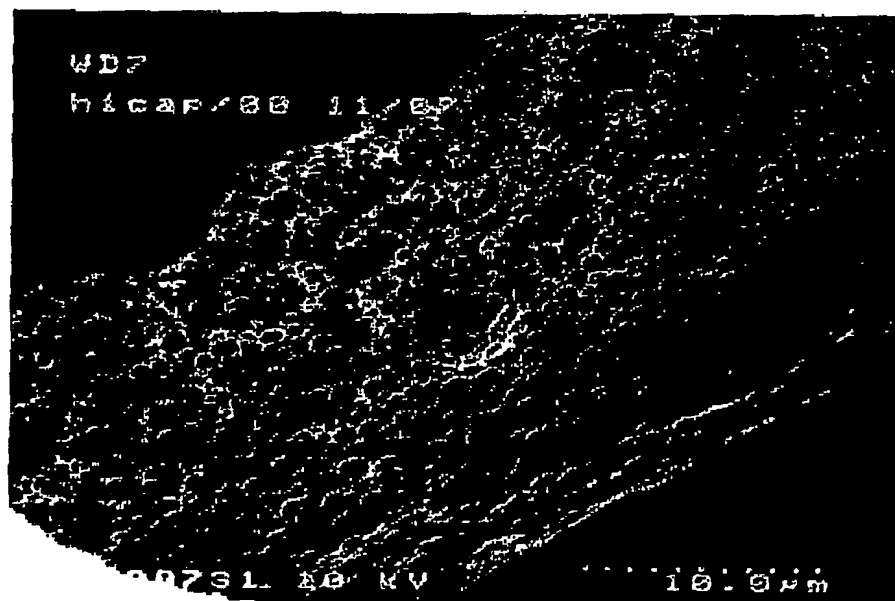
Applicant's Reference TEC 51125

4/6

Figure 7



Figure 8



Applicant's Reference TEC 51125

5/6

Figure 9

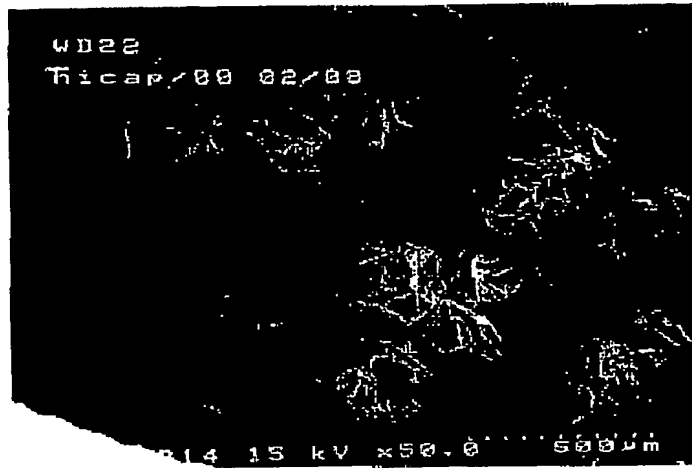
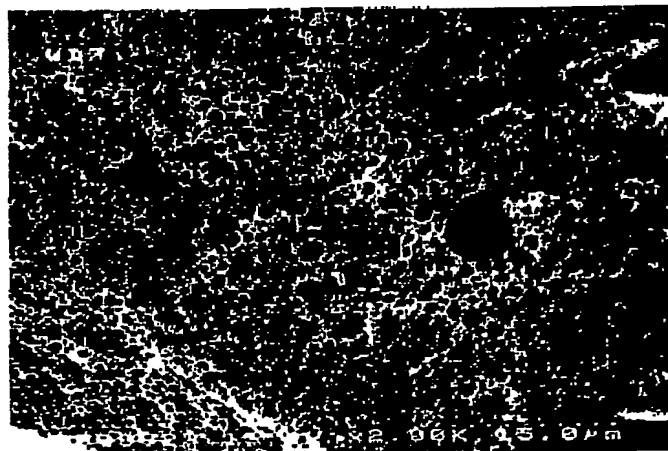


Figure 10



Figure 11



Applicant's Reference TEC 51125

6/6

Figure 12



Figure 13

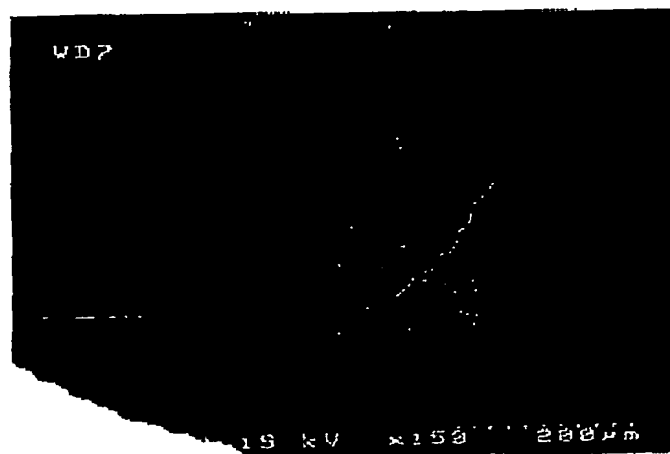
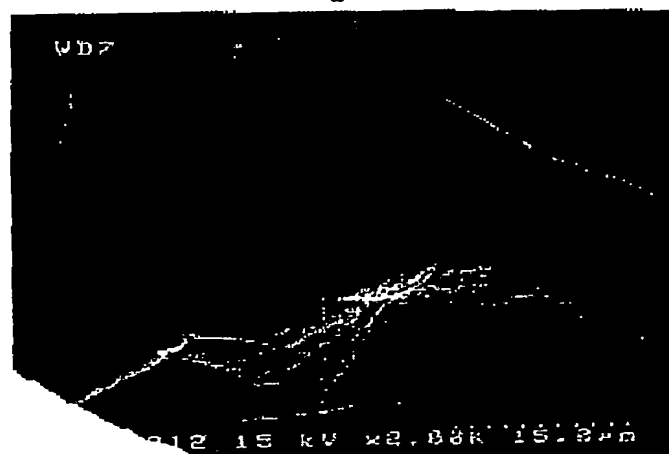


Figure 14



Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/GB04/005256

International filing date: 15 December 2004 (15.12.2004)

Document type: Certified copy of priority document

Document details: Country/Office: GB
Number: 0329208.3
Filing date: 17 December 2003 (17.12.2003)

Date of receipt at the International Bureau: 08 February 2005 (08.02.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☒ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER: _____**

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.